Quarterly Progress Report

For Period

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FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF GALLIUM PHOSPHIDE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
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Work Performed By

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PROJECT 5115: SEMICONDUCTOR DEVICES FOR HIGH TEMPERATURE USE

National Aeronautics and Space Administration
Grant NGR-05-020-043
Principal Investigator: G. L. Pearson
Staff: Anthony J. Domenico

The purpose of this project is to prepare power rectifiers and solar batteries which will operate at temperatures up to 500°C. During this quarter, the ion-pump vacuum system from Varian Associates was received, the required fixtures were fabricated, and the system was placed in operation. In addition, an undoped GaP crystal was grown in the revised vertical liquid epitaxial system and several attempts, with limited success, were made to form ohmic contacts both upon that sample and upon other GaP samples.

Vacuum System

As shown in the accompanying photographs, the work on the assembly of the "mini-vac" system has been completed. An overall view of the unit is given in Fig. 1. The top module on the right side of the table was fabricated at Stanford and contains the evaporation filament transformer and two heaters for the liquid nitrogen traps. A view of the interior of the vacuum chamber is shown in Fig. 2. As can be seen, the work fixtures have been designed for ease in the evaporation of an array of dots on the samples.

Some initial difficulty was experienced due to minor design problems which have now been overcome. For example, it was found necessary to reduce the thickness of the walls of the liquid nitrogen traps in order that the heat conduction from the top plate be lowered to an acceptable level. It was also necessary to bevel the top inner surface of the chamber itself to insure a proper fit of the top plate. These and other simlar corrections have now been made.

The performance of the system is in accordance with expectations. Due to the small volume of the chamber, the pump-down time to a pressure of $2\text{-}3 \times 10^{-7}$ torr is approximately 30 minutes, a figure several times better than previously achievable with other equipment

in this laboratory. In addition, contamination problems are lessened through the elimination of any backstreaming which would be present if an oil-diffusion vacuum system were to be used. In the coming quarters, the mini-vac system should prove to be advantageous.

Diode Preparation

As noted in the last quarterly report, some difficulty had been experienced in the attempt to grow a thin layer of undoped GaP in a hydrogen atmosphere, using the vertical epitaxial system. Further work has confirmed that the probable reason was the lack of complete saturation of the gallium solution with gallium phosphide prior to growth. Upon saturation at 15°C over the initial growth temperature of 950°C for a period of 4 hours, good results were obtained. Using a cooling program of 1/3°C per minute for four hours, a layer approximately 100 microns in thickness was grown upon a tellurium-doped GaP seed of $2 \times 10^{17} cm^{-3}$ carrier concentration.

To evaluate the quality of this grown GaP, an attempt was made to form an ohmic contact on the seed material. One face of the crystal was lapped and polished, exposing the seed material. Ni-Ge was then evaporated upon that side, and the contact was alloyed in a hydrogen reduction furnace at 650°C for 2-1/2 minutes. The results were disappointing. The contact formed was non-ohmic. The attempt was repeated twice with similar results.

To clarify the situation, a new sample of tellurium-doped GaP was divided into four parts. Two of the pieces were lapped, polished, and etched with a 2% bromine in methanol solution. The other two were similarly processed excepting a 8 $K_3 Fe(CN)_6$: 12 KOH: 100 H_2O etchant was used. Ni-Ge and Au-Ge were then evaporated on the sample such that the four combinations of surface treatments and metals were tried. Following the evaporations, the Ni-Ge samples were alloyed at 650°C for two minutes and the Au-Ge samples were alloyed at 600°C for two minutes.

The results were more promising in several respects. First of all, the 2% bromine in methanol and the 8 K_3 $Fe(CN)_6$: 12 KOH: 100 H_2O yielded essentially identical data. Secondly, the Ni-Ge contacts, although still departing from absolutely linear I-V characteristics, were superior both to those obtained in the preceding evaporation and to the Au-Ge contacts. Quantitatively, between two adjacent co-planar dots, each approximately 0.9×10^{-3} cm^2 in area, a dc resistance of 100 ohms typically was measured at a 20 milliampere current level for the Ni-Ge contacts. The Au-Ge contacts were inferior by approximately a factor of five. The Ni-Ge contacts are comparable to those previously fabricated on the vapor epitaxial GaP diodes.

However, the results are not satisfactory for a practical GaP diode. The resistance value quoted above must be lowered by greater than an order of magnitude. Therefore, our present effort is devoted to an improvement of the quality of the ohmic contacts. A program is currently being initiated to separate the effects of contact resistance and bulk spreading resistance in the semiconductor and to reduce the sheet resistivity of the evaporant suitably.

Plans for Next Quarter

Further work will be continued on the examination of the ohmic contact problem in GaP and in the growth of undoped GaP in the vertical liquid epitaxial system.

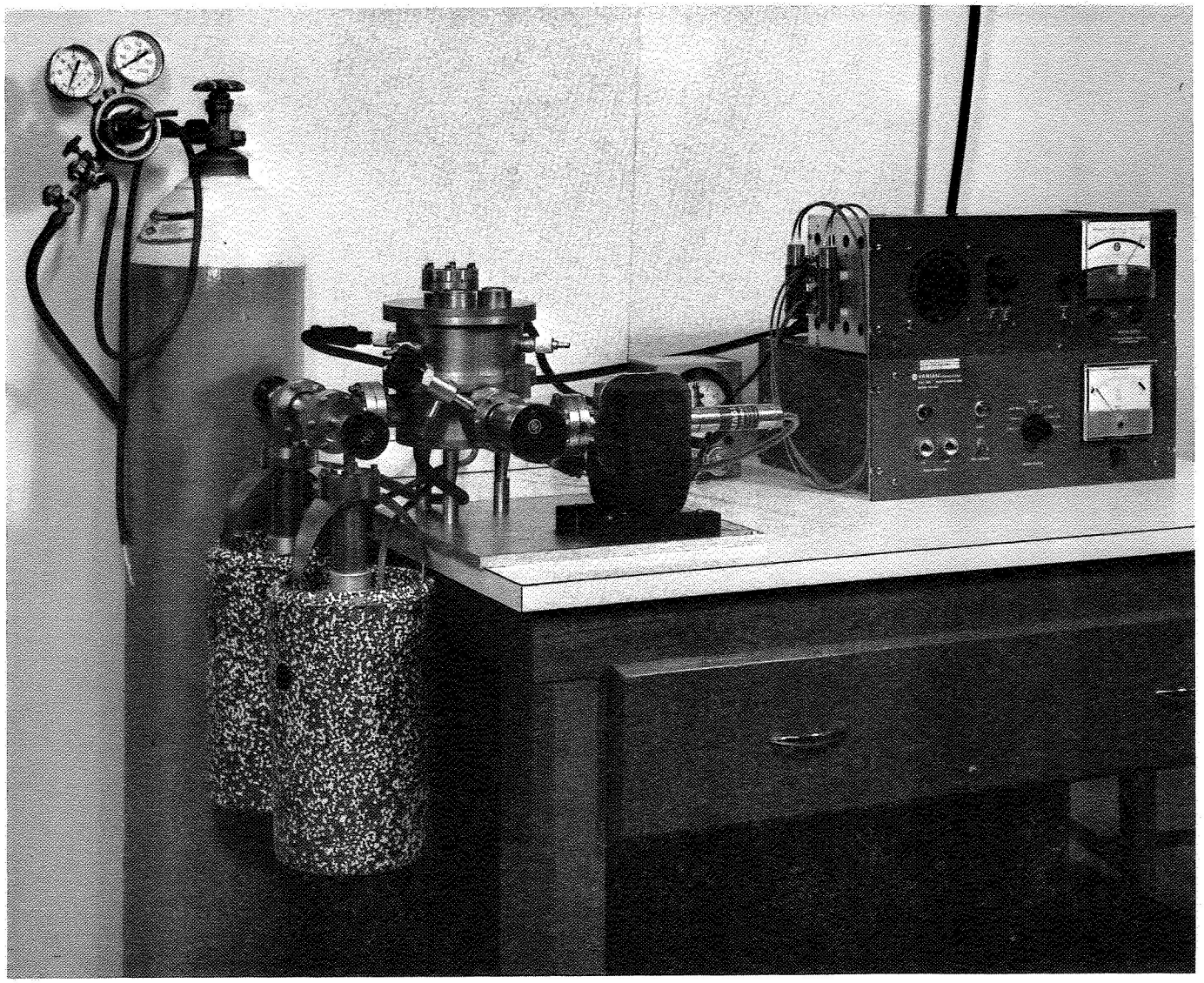

Fig. 1 An overall view of the miniature Vac Ion® system.

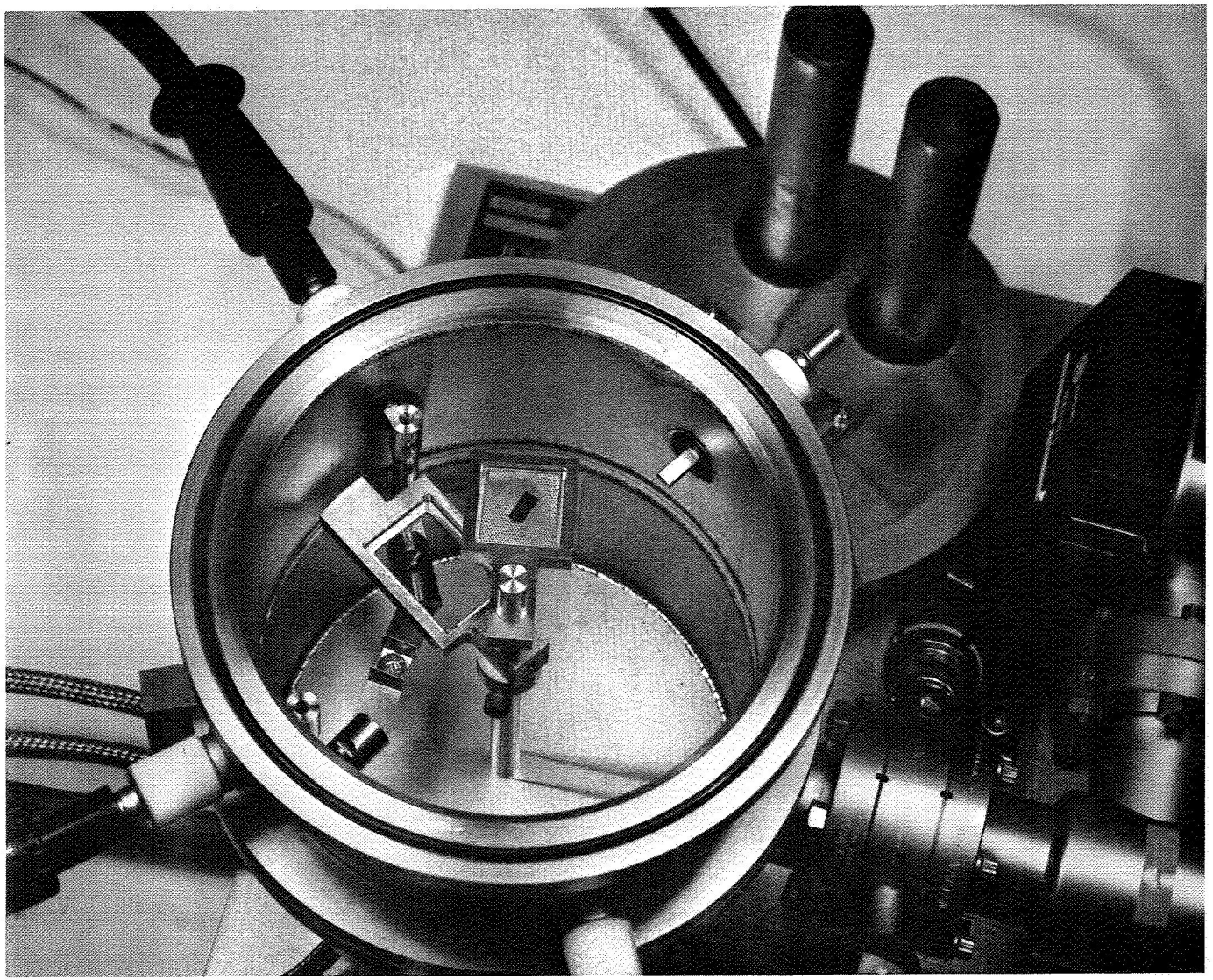

Fig. 2 The interior of the working chamber.

PROJECT 5116: DONOR IMPURITIES IN GaP

National Aeronautics and Space Administration
Grant NGR-05-020-043
Principal Investigator: G. L. Pearson
Staff: A. Young

The purpose of this project is to study the behavior of shallow donors in gallium phosphide. In particular, S, Se and Te will be diffused into GaP to determine solubility and diffusion parameters. This information will be useful in delineating the properties of GaP doped with these shallow donor impurities.

Project 5116 is now complete and will be distributed as Technical Report SEL-69-021. The abstract of this final report is given below.

ABSTRACT

The diffusion of substitutional impurities in III-V compounds has usually been explained in the literature by a model of vacancy diffusion within a single sublattice. Experimental evidence for this model, however, has been obtained solely from measurements of the temperature variation of the diffusion coefficient.

In the work reported here, a radiotracer technique was used to study the diffusion of sulfur, a substitutional donor impurity, in GaP and GaAs as a function of temperature, sulfur pressure, component pressure, and background doping of the host crystal. The importance of uniquely defining the experimental conditions has been stressed, and the necessity of elucidating diffusion mechanisms in compound semiconductors by determining the quantitative dependence of diffusion coefficient on component pressure has been emphasized. Previous reports in the literature concerning sulfur diffusion in GaAs have been inadequate in both of these respects. The diffusion of sulfur in GaP has not been reported previously.

The results reported here indicate that the variation of the diffusion coefficient with component pressure for sulfur in both GaP and GaAs is not in agreement with the model of vacancy diffusion within a single sublattice. The diffusion coefficient of sulfur in GaP was found to be independent of phosphorus pressure, whereas the diffusion coefficient of sulfur in GaAs varied as $(P_{As_4})^{1/2}$ at low arsenic pressures, and appeared to saturate at arsenic pressures greater than 0.5-1 atmospheres. The results for sulfur in GaP are consistent with diffusion via the divacancy V_{Ga}-V_P, while the diffusion of sulfur in GaAs can be explained by movement via the gallium divacancy V_{Ga}-V_{Ga}. A review of the literature indicates that the failure of the sublattice model to explain the dependence of impurity diffusion on component pressure may be a general phenomenon in III-V compounds.

The variation of solubility in III-V compounds with impurity vapor pressure has, with few exceptions, been ignored in the literature. The results reported here indicate that the dependence of surface concentration on sulfur vapor density for both GaP and GaAs is not in agreement with the usual model of incorporation of sulfur atoms on isolated anion sites. Possible reasons for this discrepancy are discussed.

Incremental Hall and plasma reflection methods were used to study the electrically active part of the impurity distribution in the diffused layers. At high concentrations, a large concentration of the sulfur was found to be electrically inactive at room temperature. This observation is of practical importance since previous reports in the literature concerning sulfur diffusion in GaAs have often assumed complete ionization of the impurities in the diffused layer. Diffusion coefficients calculated using this assumption may be in error.